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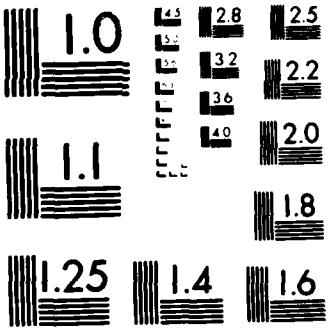


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# DIOXODODECAISOPROPOXYTETRATUNGSTEN. OXYGEN ATOM ABSTRACTION FROM ACETONE IN REACTIONS WITH HEXAISOPROPOXYDITUNGSTEN (M≡M)

by

Timothy P. Blatchford, Malcolm H. Chisholm, Kirsten Folting

and John C. Huffman

prepared for publication

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

$W_2(OPr^i)_6(py)_2$ (M≡M) and acetone (1 equiv) react in hydrocarbon solvents and ambient temperatures to yield tetramethylethylene and $(W_4O_2(OPr^i)_{12})$ which is shown, by x-ray study, to be an unusual cluster type in which the 8 electrons available for M-M bonding are partitioned to a M-M triple and M-M single bond.

Dioxododecaisopropxytetratungsten

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# Dioxododecaisopropoxytetratungsten. Oxygen Atom Abstraction from Acetone in Reactions with Hexaisopropoxyditungsten (M≡M)

by Timothy P. Blatchford, Malcolm H. Chisholm*, Kirsten Folting and John C. Huffman

(Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405, USA)

Summary $W_2(OPr^i)_6(py)_2$(M≡M) and acetone (1 equiv) react in hydrocarbon solvents and ambient temperatures to yield tetramethylethylene and $W_4O_2(OPr^i)_{12}$ which is shown, by an x-ray study, to be an unusual cluster type in which the 8 electrons available for M-M bonding are partitioned to a M-M triple and M-M single bond.

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Since their discovery the hexaalkoxides of dimolybdenum[1,2] and ditungsten[3,4] have provided entry into a rich field of reaction chemistry.[5] The metal-metal triple bonds provide a source of electrons for redox reactions and the dinuclear center may provide a template for the assembly of substrate molecules or serve to obviate the need for consecutive reduction steps. The reduction of C≡C, C≡N and C=O bonds in the reactions involving $W_2(OR)_6$ compounds exemplify these principles.[5] We describe here a reaction between $W_2(OPr^i)_6(py)_2$ and acetone which, by oxygen atom abstraction, leads to a novel tetranuclear cluster $W_4O_2(OPr^i)_{12}$.

Hydrocarbon solutions (hexane, benzene or toluene) of $W_2(OPr^i)_6(py)_2$ and acetone (1 equiv) react† according to eq. 1 at ambient temperatures.

$$2W_2(OPr_i)_6(py)_2 + 2Me_2C{=}O \longrightarrow W_4O_2(OPr^i)_{12} + 4py + Me_2C{=}CMe_2 \qquad (1)$$

Analyses of the volatiles of the reaction by $^1H$ NMR spectroscopy and g.c./m.s. showed only pyridine, tetramethylethylene and traces of acetone and isopropanol. The tungsten containing residue was obtained as black crystals from toluene and was shown to be $W_4O_2(OPr^i)_{12}$ by single crystal x-ray studies. The central $W_4O_{14}$ skeleton of the molecule is shown in Figure 1.

Though molybdenum and tungsten are known to form a wide variety of tetranuclear clusters including $M_4$ tetrahedra,[6] butterflies,[7,8] squares,[7] rectangles,[9] parallelograms[10,11] and even chains,[12] the $W_4$ skeleton seen here is unique. The average oxidation state of tungsten is +4 yielding 8 electrons for M-M bonding. Based on W-W distances,[5,13] these are evidently used to form one W-W triple bond, W(1)-W(2) = 2.404(2) Å, and one W-W single bond, W(3)-W(4) = 2.684(2) Å. Any direct M-M bonding at the distance of 2.95 Å must be weak by comparison. The molecule may thus be viewed as a dimer of dinuclear species. Note the W≡W bond is unbridged by any atom and the two tungsten atoms, W(1) and W(2), are 3 and 4 coordinate, respectively. The latter observation is very unusual and has only been seen recently in $(Pr^iO)_3Mo{\equiv}Mo(OPr^i)(CH_2Ph)_2(PMe_3)$.[14] The oxo bridges may be partioned: O(5) as $O^-$ to W(1), i.e. O(5) is like an alkoxy group in which W(3) substitutes for a carbon atom, and O(6) as an oxygen dative bond to W(2). Consistent with this line of reasoning W(3)-O(5) = 1.86(2) and W(3)-O(6) = 2.01(1) Å representing formally W-O double and single (dative) bond distances, respectively. The other half of the molecule involving W(3) and W(4) is a confacial bioctahedron, $(RO)(O^-)(O^{2-})W(\mu\text{-}OR)_3W(OR)_3$, containing a $W_2^{10+}$ core:(M-M).

The oxygen atom abstraction reaction and coupling of ketonic carbon atoms in eq. 1 has an obvious parallel with the McMurray reagent[15] which employs reduced titanium, probably finely divided Ti metal or at least clusters.[16] In the present instance it is probable that C-C bond formation occurs to give a diolate, akin to the reactions reported by Cotton and Walton and their co-workers[17] involving W=W bonds. From here the reaction could proceed to give C-O bond cleavage and the alkene followed by cluster formation or alternatively the reaction with $W_2(OPr^i)_6$, as a reducing agent, could give a $W_4$-cluster from which alkene is released.

Further studies aimed at elucidating the mechanism of this reaction and evaluating its scope toward organic syntheses are planned.[18]

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†Dry and oxygen free atmospheres ($N_2$) and solvents were used throughout.

+Crystal data for $W_4O_2(OPr^i)_{12}$ at -140°C: a = 13.386(7) Å, b = 19.426(15) Å, c = 10.250(6) Å, $\alpha$ = 99.28(4)°, $\beta$ = 104.20(3)°, $\gamma$ = 94.52(3)°, Z = 2, $d_{calcd}$ = 1.938 g cm$^{-3}$ and space group $P\bar{1}$. Of the 6658 unique reflections collected using Mo $K_\alpha$, $6° \leq 2\theta \leq 45°$, the 5423 having $F > 3\sigma(F)$ were used in the full matrix least-squares refinement, using anistropic thermal parameters on the W atoms, while O and C atoms were isotropic. The hydrogen atoms were located in fixed positions. No absorption or extinction corrections were used. There was no evidence of solvent molecules being present. Final residuals are R(F) = 0.065 and Rw(F) = 0.065. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical

Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The complete structure report, MSC No. 84036, is available from the Indiana University Library in Microfiche form only.


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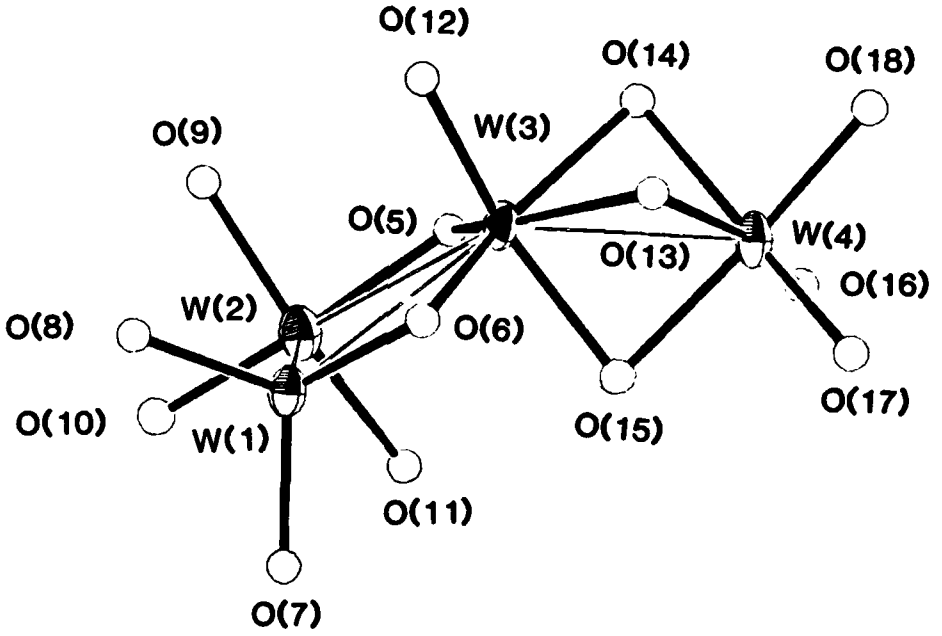
## Caption to Figure

Figure 1. The central $W_4O_{14}$ skeleton of the $W_4O_2(OPr^i)_{12}$ molecule. O(5) and O(6) are oxo oxygen atoms. Some pertinet distances (Å) and angles (°) are: W(1)-W(2) = 2.404(2), W(1)-W(3) = 2.948(2); W(2)-W(3) = 2.950(2); W(3)-W(4) = 2.684(2); W(1)-O(6), -O(7), -O(8) = 1.845(13), 1.865(14), 1.856(13); W(2)-O(5), -O(9), -O(10), -O(11) = 1.942(13), 1.910(16), 1.883(17), 1.951(16); W(3)-O(5), -O(6), -O(12), -O(13), -O(14), -O(15) = 1.857(13), 2.008(13), 1.902(14), 2.197(13), 2.125(14), 2.055(13); W(4)-O(13), -O(14), -O(15), -O(16), -O(17), -O(18) = 2.016 (13), 2.054(14), 2.054(13), 1.888(17), 1.910(15), 1.805(14); W(2)-O(5)-W(3) = 101.9(6), W(1)-O(6)-W(3) = 99.8(6); W(2)-W(1)-O(6) = 108.1(4); W(2)-W(1)-O(7) = 105.2(4), W(2)-W(1)-O(8) = 106.9(4); W(1)-W(2)-O(5) = 103.9(4); W(1)-W(2)-O(9) = 101.1(5); W(1)-W(2)-O(10) = 99.9(5); W(1)-W(2)-O(11) = 102.5(5); W(1)-W(2)-W(3) = 65.91(5); W(2)-W(1)-W(3) = 65.98(5); W(1)-W(3)-W(2) = 48.11(4); W(1)-W(3)-W(4) = 137.48(5); W(2)-W(3)-W(4) = 131.50(5).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